APPENDIX D

LIFE CYCLE MANAGEMENT OF SHOCK SENSITIVE CHEMICALS

Introduction and Scope:

The purpose of this appendix to the DOE Chemical Management Handbook Volume 1 is to heighten complex wide awareness and concern for the safe lifecycle management of shock sensitive chemicals. It provides an overview of this subject. For specific information on the management of shock sensitive chemicals, consult the listed publications at the end of this appendix and qualified professionals.

Background:

Shock sensitive chemicals are those chemicals that may explode with impact, movement or handling, friction or heat. These chemicals have the potential to undergo a rapid, uncontrolled reaction that may be violent enough to produce an explosion.

There are two types of shock sensitive chemicals. Some chemicals are inherently shock sensitive. These materials have known hazards, predictable properties and may be governed by various codes and standards. The other group of shock sensitive materials is those compounds that initially are not shock sensitive but become so due to chemical changes, such as those from improper or prolonged storage. Properties of these materials are unknown, unpredictable and these additional hazards may or may not be identified on the Material Safety Data Sheet (MSDS) of the parent chemical. Mechanisms causing chemicals to become shock sensitive upon chemical changes from improper or prolonged storage include drying, decomposition, and slow reactions with oxygen, nitrogen, or the container.

Incidences and Causes:

The following are examples of the numerous reports of incidents involving shock sensitive chemicals. Note that both of these incidents involved chemicals that became shock sensitive upon prolonged storage.

A technician used a pair of channel lock pliers to twist the rusty lid off a small, dark green bottle to characterize the unknown chemicals inside. There was an immediate explosion and glass shards embedded in a nearby chair. Analysis showed that over time the picric acid in the bottle combined with the metal lid to form shock sensitive metal picrates that lodged in the threads in the neck of the bottle.

A technician was remotely handling an old, opened, metal can of anesthesia grade ethyl ether to add more ethyl alcohol as an inhibitor. Enough inhibitor was thought to be present, so the ether was not considered hazardous. The liquid level in the can was low so the technician had to tilt the can to pipette out an aliquot for the peroxide test strip. As the technician turned the can upright, an explosion occurred and a fireball filled the fume

hood. The slight handling of the can was enough of a mechanical shock to cause peroxide crystals in the top portion of the can to explode.

EXAMPLES OF SHOCK SENSITIVE CHEMICALS

Classes of Inherently Shock Sensitive Chemicals:

Azides:
- Silver azide,
- Organic azides,
- Metal azides,
- Nonmetal azides
  - ($-N_3$ or N_3^-)

Acetylides of heavy metals:
- Copper, silver, and mercury salts
- (-CCH)

Amine oxide:

- ($=N^+-O^-$)

Chlorate:
- Ammonium perchlorate
- ($Cl0_3^-$)

Chlorite Salts:
- Silver chlorite
  - ($Cl0_2^-$)

Diazo:
- Diazomethane,
- (-N=N-) Diazonium salts (when dry),
- benzene diazonium chloride
- ($-N_2^+$)

Fulminates:
- Fulminating Silver
- (ONC^-)

Haloamines:
- Chloro benzyl amine
- (-NHX)

Hydroperoxide:
- Cumene Hydroperoxide
- (-OOH)

Hypohalite:
Iodoform
(OX^-)

Nitrate salts or esters :
Ammonium nitrate,
Guanidine nitrate
(NO_3^- or $-ONO_2$)

Nitrite salts or esters:
(NO_2 or -ONO)

Nitro compounds:
nitrocellulose
($-NO_2$)

Nitroso;
Dinitrosylnickel
(-NO)

Oxidizers:
Ammonium perchlorate,
Ammonium permanganate

Organic Peroxides:
Benzoyl peroxide (over 98%),
t-Butyl hydroperoxide (over 90%),
di-isopropyl peroxydicarbonate (100%)

Ozonide:
trans-2-Butene ozonide
($-O_3^-$-)

Peracid:
Performic acid
$R-CO_3H$

Perchlorates:
Potassium perchlorate
$-ClO_4^-$

Polynitroaromatics:
Picric acid,
TNT

Metal Picrate:
Copper picrate,
Transition and heavy metal picrates such as nickel, lead, mercury, zinc

Classes of Chemicals that may become Shock Sensitive:

Acrylates or Methacrylates:
Methyl methacrylate

Aldehydes:
Acetaldehyde

Alkanes and Cylcoalkanes with tertiary Hydrogen:
Cyclohexene

Alkenes with alyllic Hydrogen:
2-ethyl-1-pentene

Alkylalkyenes with alpha Hydrogen:
Isopropyl benzene,

Alkylalkyenes with tertiary alpha Hydrogen:
Ethylcyclohexane

Dienes:
Butadiene,
Chloroprene

Ethers and Acetals with an alpha Hydrogen:
Diethyl ether,
Di-isopropyl ether,
Dioxane,
Tetrahydrofuran

Fluoro or Chloroalkenes:
tetrafluoroethylene

Ketones with alpha Hydrogen:
dilsopropyl ketone

Secondary Alcohols:
DiPhenylmethanol

Ureas, amides and lactams with alpha Hydrogen on a carbon attached to nitrogen:
N-ethylacetamide,
N-isopropylacetamide

Vinyl halides, esters or ethers:
Vinylidene chloride,
Vinyl chloride,
Vinyl acetate)

Vinylalkynes with alpha Hydrogen:
diAcytylene,
Vinylacetylene

Note: some chemicals such as secondary alcohols will form explosive peroxides but these products need to be evaporated to dryness before the explosion hazard manifests itself.

The lists above are only examples. Not all members of the above classes may be or may become shock sensitive. Likewise, some chemicals in classes not listed above may be or may become shock sensitive. **Currently there is no available methodology that would allow DOE to create a definitive definition and/or list of shock sensitive or potentially shock sensitive chemicals.** Additional lists of chemicals or chemical classes of shock sensitive chemicals have been published (2, 4, 5, 12, 15, 23).

A critical part of managing the life cycle of shock sensitive chemicals involves the identification of those chemicals (see below).

Handling and Use:

Respect the chemical and the dangers it presents

If you find chemicals that are or have the potential of becoming shock sensitive and they are outdated (expired shelf life), suspect, or show signs of degradation, immediately contact your supervisor and your organization's ES&H or Hazardous Materials department.

DO NOT TOUCH OR MOVE SUSPECT CHEMICALS!

When working with shock sensitive chemicals

Make sure that you have access to the MSDS, the chemical is labeled as required by your facility, and the container is entered into your facility's hazardous chemical management program. Study the chemical's MSDS and label. Look for information about the chemical's reactivity, stability and hazards. If there is an NFPA diamond or an Hazard Material Information System (HMIS) label, look for a 2, 3, or 4 in the yellow "Instability" (formerly Reactivity) section or a ~~W~~ (water reactive) in the white "Special Hazards" section.

Closely follow approved work procedures and hazard controls. Review information from other chemical safety resources. Check with your facility's chemical safety personnel. Use appropriate personal protective equipment (PPE). Protect the chemical from shock, friction or heating.

Standards and Codes:

29CFR1910.1200 – 'Hazard Communication'
Reactive hazards must be noted on the MSDS.

29CFR1910.1450 – 'Occupational Exposure to Hazardous Chemicals in Laboratories'
The chemical hygiene plan should address shock-sensitive hazards.

NFPA 45 - 'Standard on Fire Protection for Laboratories Using Chemicals'

NFPA 432 - 'Code for the Storage of Organic Peroxide Formulations'

NFPA 430 – 'Code for Storage of Liquid and Solid Oxidizers'

NFPA 704 - 'Standard System for the Identification of the Hazards of Materials for Emergency Response'

See the DOE Handbook on 'CHEMICAL MANAGEMENT' (Volume 3 of 3) 'Consolidated Chemical User Safety and Health Requirements' for a detailed compilation of all requirements.

http://tis.eh.doe.gov/techstds/standard/hdbk1139/hdbk11392003vol3.pdf

Chemical Lifecycle Management:

Management Support

Management needs to understand liabilities associated with shock sensitive chemicals and support those programs necessary for the management of these chemicals. Management also should develop clear roles responsibilities and authorities so that various aspects of chemical management are never in question.

Training and Qualifications

Management should ensure that employees who handle, store, or use shock sensitive chemicals are trained to understand the hazards and trained to recognize when a potentially shock sensitive chemical has become "unsafe".

When shock sensitive, unstable compounds are found they should only be handled by trained, qualified specialists as identified by management.

Identification of Shock Sensitive and Potentially Shock Sensitive Chemicals

The most important element of a shock sensitive chemical management program is to determine how shock sensitive and potentially shock sensitive chemicals will be identified. Since there is no definitive answer as to what should or should not be defined

and managed as being shock sensitive, written guidance should be developed. This guidance should take into account the type of work being performed, the nature of the chemical in question, storage conditions, other safety systems present, etc., and should be implemented by a qualified person designated by management. It should also be made available to all employees and the employees should be encouraged to question any determinations that do not appear to be valid.

Acquisition Control

Experiments and processes should be planned appropriately so that necessary quantities can be procured. With "Just-In-Time" contracting, shock sensitive chemicals can be obtained within a short period. This could be used to meet the needs of chemical workers while keeping inventories of shock sensitive chemicals to a minimum. Using "Just-In-Time" contracting essentially causes the chemical supplier to become the storage facility for one's shock sensitive chemicals.

Just-In-Time contracts usually consist of agreements with suppliers that provide for a firm delivery time. This time, coupled with internal delivery time, allows the worker to plan ordering lead-time in order to have the chemicals arrive just prior to needing them. These materials are usually ordered with slight excess and any left over materials should be disposed of to reduce the potential for aging inventories (leftover reagent) in storage.

Consider purchasing peroxide formers with inhibitors if possible.

Tracking of Shock Sensitive Chemicals

Once a chemical is determined to be shock sensitive or have the potential of becoming shock sensitive over time, it should be tracked in a data system. Data elements should include each container's contents, container owner, amount, location, date received, date opened, and last date inspected and/or next inspection date. If this information is not available, then the container cannot be found and inspected at the required time and properly managed.

Defining Storage Conditions

Different chemicals have different storage needs and these needs should be clearly defined. The first reason for this is to prevent incorrect storage conditions that could result in hazardous situations. Some conditions such as exposure to heat, light, air, and humidity can aid reactions that cause chemicals to become shock sensitive. Other conditions such as refrigeration can cause the inhibitor to become ineffective and allow peroxide formation.

A second reason to define storage conditions is to articulate policy concerning the storage of shock sensitive and potentially shock sensitive chemicals.

Defining Inspection Period

Because all chemicals are not the same, inspection periods need to be adjusted for each chemical. Storage conditions should also be included in determining the inspection frequency. An important part of managing time-sensitive chemicals is to determine appropriate inspection periods for each chemical in the program. Inspection periods for each chemical should be defined as a part of the organization's chemical management program. NFPA 45 requires the inspection of these types of chemicals in a laboratory every 6 months. However, some peroxide formers that may become shock sensitive, such as di-isopropyl ether, should be inspected and tested, at a maximum, every 2 weeks.

Do not assume that a new, recently purchased, unopened chemical is safe. It is not uncommon to receive "potential peroxide forming chemicals", which have already formed unsafe levels of peroxides.

Defining "Unsafe"

As chemicals are inspected, there needs to be a definition as to what constitutes "unsafe". If "unsafe" is not defined, then one cannot determine when a container fails inspection. It is important to note that some measurements such as peroxide determinations can be inherently low. To prevent dangerous levels of peroxide, a routine monitoring program should be put in place to watch the trend of peroxide concentrations. Once peroxide formation has started it will tend to accelerate at a nonlinear rate and the container should be disposed as waste immediately.

Managing "Unsafe" Chemicals

Once a chemical or waste stream has become unsafe due to dehydration, solvent evaporation, or the formation of hazardous products, processes used to manage the material must be clearly defined in the chemical management program. Employees need to know if they call the professional expert designated by management, if they are to call the bomb squad or emergency response, etc.

Reference Material:

1. Bailey, J., Blair, D., Boada-Clista, L., Marsick, D., Quigley, D., Simmons, F., Whyte, H., "Management of Time Sensitive Chemicals (I): Misconceptions Leading to Incidents", *Chemical Health & Safety*, Vol. 11, No. 5 (to be published Sept/Oct 2004).
2. Bailey, J., Blair, D., Boada-Clista, L., Marsick, D., Quigley, D., Simmons, F., Whyte, H., "Management of Time Sensitive Chemicals (II): Their Identification, Chemistry, and Management", *Chemical Health & Safety*, Vol. 11, No. 6 (to be published Nov/Dec 2004).
3. United States Department of Justice, Federal Bureau of Investigation, Bomb Data Center, Technical Bulletin Dated November 10, 1982, "Warning: Picric Acid – San Mateo County, California", Washington, D.C.

4. Kelly, R. J.,"Review of Safety Guidelines for Peroxidizable Organic Chemicals", *Chemical Health & Safety,* Vol. 3, No. 5, Sept./Oct., 1996, pgs. 27-36.
5. Clark, Donald E., "Peroxide and Peroxide-forming Chemicals", American Chemical Society, *Chemical Health & Safety*, Sept./Oct., 2001, Pgs.12-21.
6. Steere, Norman V., "Control of Hazards from Peroxides in Ethers", Journal of Chem. Ed., Vol. 41, No. 8, August, 1964.
7. Davies, Alwyn G., "Explosion Hazards of Autoxidized Solvents", Journal of the Royal Inst. of Chem., Vol. 80, pgs.386-389.
8. Turk, E., "Phosgene from Chloroform", *Chem. Eng. News*, 1998, 76(9), 6
9. BBC News Article, Published 07/21/2003, http://news.bbc.co.uk/go/pr/fr/-/2/hi/uk_news/england/tyne/wear/3083899.stm
10. Princiotto, Laurie A, <lprincio@INDIANA.EDU>, "Hydrogen Fluoride Cylinder Ruptures", Laboratory Safety Specialist, Indiana University, Dept. of Environmental Health and Safety, Creative Arts Building, Bloomington, IN., 47408-2602, http:www.ehs.indiana.edu.
11. SET Environmental, Inc., Hydrogen Bromide Safety Advisory, Houston, Texas, January 23, 2003.
12. Mirafzal, G. A.; Baumgarten, H. E., "Control of Peroxidizable Compounds: An Addendum", *J. Chem. Ed*. 1988, 65, A226.
13. Sharpless, T.W., "Butanol Safety Hazard", *J. Chem Ed*. 1984, 61, 47.
14. Jackson, K. L.;McCormack, W. B.;Rondestvedt, C. S; Smeltz, K. C.; Viele, I. E., "Control of Peroxidizable Compounds", *J. Chem. Ed*. 1970, 47(3), A175-88.
15. Recognition and Handling of Peroxidizable Compounds: Data Sheet 655; National Safety Council: Chicago, IL, 1976,1982, and 1987.
16. Standard Test Methods for Assay of Organic Peroxides: ASTM E 298-91, ASTM Subcommittee E15.22, May 1991.
17. Meites, L. *Handbook of Analytical Chemistry*; McGraw-Hill; New York, 1963; p. 12-113 (Table 12-43).
18. *Encyclopedia of Chemical Reactions*; Jacobson, C. A., Ed.; Reinhold: New York, 1958; Vol. 7, p.411.
19. E. Merck/EM Science, Merckquant Peroxide Test Strip, Postfach 41 19, D6100 Darmstadt, Germany; EM Science, 480 Democrat Rd., Gibbstown, NJ 08027; 609-354-9200.
20. Brethrick, L., *Bretherick's Handbook of Reactive Chemical Hazards*, *4th ed*; Butterworth-Heinemann Ltd: Oxford, 1990.
21. Ashbrook, P. C., Houts, T. A.; "Laboratory Waste Minimization, Chemical Waste Disposal Costs", *Chem. Health Safety*. 2003, 10, 32.
22. National Research Council, *Prudent Practices in the Laboratory: Handling and Disposal of Chemicals*: National Academy Press; Washington, D.C., 1995.
23. Merck & Co., Inc., *The Merck Index: 13th ed*.: Merck Research Laboratories, Whitehouse Station, NJ, 2001.
24. Lewis, R. J., *Sax's Dangerous Properties of Industrial Materials, Vol. 2: 8th ed*.: Van Nostrand Reinhold, New York, 1992.
25. Karrer, P., *Organic Chemistry: 4th ed*.: Elsevier: New York, 1950.
26. Rodd, E. H., *Chemistry of Carbon Compounds, Vol. 1*: Elsevier: New York, 1951.

27. Huntress, E. H., *The Preparation, Properties, Chemical Behavior, and Identification of Organic Chlorine Compounds*: John Wiley and Sons: New York, 1948, p. 550.
28. Watson, E. F., "Anhydrous Hydrogen Flouride", *Chem Eng. News*, 1997, 75(17), p 6.
29. *Environmental Health and Safety News Article71: Hydrogen Fluoride Cylinder Hazard*: University of Maryland, July 16, 1999.
30. *Hazards in the Chemical Laboratory, 3rd Ed*. Royal Society of Chemistry, 1981.
31. Meyer, E.: *The Chemistry of Hazardous Materials, 2nd ed*., 1989, Prentice Hall, Englewood Cliffs, New Jersey.
32. DOE Chemical Management Handbook Volumes 1 - 3: http://tis-nt.eh.doe.gov/web/chem_safety/library/Doe_reg.html
33. The Society of the Plastics Industry – Organic Peroxide Producers Safety Division: http://www.plasticsindustry.org/about/organicperoxide.htm
34. DOE Explosives Safety Manual (M440.1-1) http://www.directives.doe.gov/pdfs/doe/doetext/neword/440/m4401-1.html
36. The Society of the Plastics Industry – Organic Peroxide Producers Safety Division: http://www.plasticsindustry.org/about/organicperoxide.htm
37. ES&H Bulletin EH-91-2 "Safe Chemical Storage" http://tis-hq.eh.doe.gov/docs/bull/bull0062.html